

An approach to provide maps of the N2O emission risks by soils at the regional scale: A case-study at the Haut-Loir watershed, France

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1	Title:
2 3	An approach to provide maps of the N_2O emission risks by soils at the regional scale: a case-study at the Haut-Loir watershed, France
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15	Highlights:
16	A methodology is developed to map N ₂ O emission risk based on soil properties.
17	The hazard and the vulnerability allow inferring the risk of N ₂ O emissions
18	This methodology is relevant for all types of soil dedicated to agriculture
19	Areas where N ₂ O emissions mitigation actions are possible have been identified.
20	
21	Abstract:
22	Nitrous oxide (N ₂ O) is often emitted by soils after nitrogen fertilization when the reduction of nitrate
23	into N_2 is incomplete and the soil is in hydromorphic condition. To take action to reduce N_2O
24	emissions, it is necessary to identify and locate areas that present a risk of N ₂ O emissions. In this
25	study, an approach to map N_2O emission risk by soils was therefore developed based on soil
26	properties. The risk of N ₂ O emission was assessed through two components linked to static properties,
27	independent on climate and agricultural practices; the Vulnerability: the ability of the soil to reduce
28	N ₂ O and the Hazard: the probability of soil water-logging. This approach was tested in the Haut-Loir
29	watershed (3600 km ²), a highly cropped area in the French Center Region. Vulnerability and hazard
30	were estimated using French soil databases. The databases contain the drainage class information

which allowed inferring the hazard. They also have measurements of pH, CEC and clay content which

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32 allowed estimating vulnerability through a pedotransfer function. In this watershed, contrasting risks were highlighted between different soil types and agricultural regions. High risk soils (~2% of the 33 34 studied area) were generally found in valleys and were not under crop because of their hydromorphy 35 and acidity. However, attention should be given to medium risk soils (~32% of the area) which were mainly found in the western region. Oppositely, soils of the eastern region present generally no risk of 36 37 N₂O emissions. Some former field studies have been reported in the studied watershed: they generally 38 supported this soil risk classification. For medium-risk soils, different actions of mitigation depending 39 on the degree of risk were suggested: liming or adjusting nitrogen input periods. This risk mapping 40 approach could be applied in other cropland regions to help mitigation strategy.

41

42 Keywords:

Greenhouse gas; Risk assessment; Vulnerability; Hazard; Exposure; Soil mapping; Multiple soil
 classes.

45

46 Abbreviations:

47 CEC, Cation Exchange Capacity; GHG, Greenhouse Gas; HV, High Vulnerability; HH, High Hazard;
48 HR, High Risk; IPCC, Intergovernmental Panel on Climate Change; Km, Kilometers; LV, Low
49 Vulnerability; LH, Low Hazard; LR, Low Risk; MM, Moderate Vulnerability; MH, Moderate Hazard;
50 MR, Moderate Risk; RP (French), Pedological Referential; RRP, Pedological Regional Referential;
51 STU, Soil Typological Units; SMU, Soil map Units; WRB, World Reference Base for soil resources.
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55 1. Introduction

56 Climate change induced by increased Greenhouse Gases (GHGs) emissions in the atmosphere results 57 in global warming (Masson-Delmotte et al., 2018). Nitrous oxide (N₂O) is one of the three main 58 anthropogenic GHGs in the atmosphere. N₂O has about 265 times the warming potential of CO_2 (Ciais 59 et al., 2013), but its concentration is more than 1000 times lower than atmospheric CO_2 concentration, 60 so its contribution to the greenhouse effect is evaluated for 2020 at about 7% against 66% for CO₂ and 61 16% for CH₄ (WMO, 2021). In France, agriculture is the main sector contributing to anthropogenic N₂O emissions and represented about 89% of these emissions in 2019 (Thompson et al., 2019; 62 CITEPA, 2021). Agricultural emissions of N₂O are mainly due to N inputs of mineral and organic 63 64 fertilizers in soils and a linear relation is assumed between N inputs and N₂O emissions (1% of N 65 input, IPCC Tier-1, Hergoualc'h et al., 2019). In France, since 1990, N₂O emissions have been slightly 66 decreased, from 65.4 to 38.2 Mt CO₂e, and emission due to agriculture decreased slowly from 38.2 to 34.5 Mt CO₂e (CITEPA, 2021), thanks to the use of more optimized and regulated mineral fertilizers. 67 68 The "Centre - Val de Loire" region is a region of intensive agriculture where the contribution of 69 agriculture to total N₂O emissions is estimated to be as high as 95% (2.6 Mt CO₂e) corresponding to 70 about 14% of all GHGs in CO₂e (LIG'AIR inventory V2.4/2020).

71 Agricultural N₂O emissions exhibit a very large spatial and temporal variability because they are 72 highly dependent on pedoclimatic conditions (e.g., soil concentration of mineral nitrogen, soil 73 moisture, temperature). The N₂O is indeed produced by several microbial processes resulting from the 74 activity of different species of microorganisms (e.g., nitrification, denitrification, nitrifier 75 denitrification...; Butterbach-Bahl et al., 2013) using soil nitrogen as substrate. Denitrification (the 76 reduction of nitrate in several steps, to N_2O and lastly to N_2) is considered as one of the most 77 important processes of N₂O production in soils (Dobbie and Smith, 2001). Denitrification occurs in 78 anoxic soils and is therefore favored by soil moisture. Large peaks of N₂O emissions occur in wet soils 79 with high nitrogen (N) levels, usually after input of nitrogen fertilizers (Stehfest and Bouwmann, 80 2006; Ito et al., 2018). Complete denitrification leads to N₂ emission, which is not of environmental 81 concern since N₂ is a non-reactive molecule and is not absorbing in the infrared spectrum. The last 82 step of denitrification, the reduction of N₂O in N₂, is inhibited in certain soil conditions or in some soils. Therefore, some soils do not present a capacity to reduce N₂O to N₂. For example, pH controls 83 84 the ability of the denitrifying bacteria to express N₂O reductase early and efficiently (Russenes et al., 85 2016), which probably explains why soil pH influences N_2O emissions when denitrification is the main source of N₂O. Previous studies also revealed soil pH as one of the main factors governing 86 87 regional variability of N_2O emission on a global meta-analysis (Wang et al., 2018). Many studies have 88 been conducted to understand the determinism of N₂O production and reduction, bringing more and 89 more insight into these processes and their controlling factors (Stehfest and Bouwman, 2006; Cui et 90 al., 2021) and the effect of different agricultural practices. This enables to propose some technical 91 solutions to limit N₂O emissions. Avoiding excess soil nitrate, particularly when soils are too wet, can 92 help minimize N₂O emissions from agriculturally managed soils. Other solutions are being studied, 93 like bacterial seeding, draining moist soil, nitrification-inhibiting (e.g. Henault et al., 1998; Rochette, 2008; Ruser and Schulz, 2015; Hinton et al., 2015). pH management, i.e. soil liming to raise the pH, is 94 95 also an important track to reduce N₂O emissions (Henault et al., 2019; Shaaban et al., 2020).

96 However, most studies have been made at field scale, so the representativeness of observations when 97 upscaling (e.g. regional scale) is unclear. N₂O is indeed produced at soil microsite scale and this 98 production is controlled by a complex interaction of factors. Therefore, similar agricultural practices 99 can have different effect on N_2O emission in different soil types (e.g. Rochette et al., 2008). The use of 100 methods to reduce N₂O emissions involve identifying soils which are likely to emit N₂O. This is 101 consistent with the findings of Cui et al. (2021), who recently provided a global map of N_2O emission 102 factors (i.e. N₂O emission taking into account nitrogen inputs) based on a data-driven meta-analysis. 103 They outlined that the most policy-relevant question is to identify where emissions can be mitigated 104 more efficiently.

105 It is therefore useful to provide maps of N_2O emissions or emission risk which can indicate where 106 actions have to be taken. Few studies provide spatial assessment of emissions and they generally 107 consider agricultural practices, which can be difficult to obtain. Mapping N_2O emission can be done 108 by applying predictive models: this approach was used by the European Soil Data Centre, who

109 published a map of N₂O emissions from agricultural soil in Europe taking soil properties into account, 110 based on LUCAS soil sampling program and using DayCent model combined with random forest 111 approach (Lugato et al., 2017). The resulting map depends on climatic data inputs and information on 112 managements practices. As N₂O emissions are extremely dependent on climatic conditions, they 113 averaged 5 years of data to smooth the temporal variability. Another method was proposed by Kritee 114 et al. (2018) who mapped risk of large N₂O emissions from rice production taking into account two 115 components: water management regimes and regional N fertilizer rates, but ignoring soil properties. In 116 both cases, the maps are a snapshot of a given situation as climate and management practices are 117 subjected to change. Providing soil N₂O emission risk, based on soil properties, i.e. static or more or 118 less static properties, is a valuable approach for policy-makers. This is consistent with the approach of 119 Cui et al. (2021): they provided a global map of emission factors rather than N_2O emissions. Global 120 information may however have a too coarse resolution for defining mitigation strategies; the best scale 121 would be regional or national, which is also the scale of policy-making. However, Cui et al. (2021) 122 also observed that controlling factors are scale-dependent, so it is very important to further provide 123 regional maps of N₂O emission risk.

124 The objective of this paper was therefore to develop an approach to map at regional scale N₂O 125 emission risk based on soil properties. IPCC approach defined risk as the likelihood of harmful 126 alterations due to hazardous physical events interacting with vulnerable conditions (Lavell et al., 127 2012). They proposed to cross hazard, vulnerability and exposure to fully assess risk, and defined these three notions. Hazard is the potential occurrence of a physical event having adverse effect; 128 129 vulnerability is the predisposition of an element to be affected due to internal characteristics; and 130 exposure referred to the presence of resources in places that could be affected by the physical events. 131 A similar approach is then developed here for N_2O emission risk. Hazard was considered as soil water 132 excess probability, which leads to conditions favorable to denitrification. Vulnerability was considered 133 to be due to the soil capacity to reduce N₂O in N₂, which, as already mentioned, depends on soil 134 properties. Exposure corresponds to soil nitrogen inputs. In this study, vulnerability and hazard were 135 considered simultaneously to provide maps considering only static risk in relation to soil properties.

136 Soil capacity to reduce N_2O to N_2 can be evaluated in the laboratory, using incubated soil samples according to ISO/TS 20131-2 method (Le Gall et al., 2014; Henault et al., 2019). An index, called r-137 138 max value, is calculated, which corresponds to the ratio between the amount of N_2O emitted without 139 and with acetylene during incubation because acetylene inhibits the last step of denitrification. The higher is the r-max, the lower is the soil's ability to reduce N₂O to N₂. The r-max value can also be 140 141 estimated by a soil function depending of pH, Cation Exchange Capacity (CEC) and clay content, 142 where pH is the more relevant variable of function (Henault et al., 2019). This function was applied on 143 soil databases. Hazard was assessed by the natural soil hydromorphic class.

144 Providing N₂O emission risk assessment is especially important in intensive cropland areas receiving 145 large fertilizations. The present approach was thus applied in an intensive cropland region of France. 146 The first step was to map the r-max index using the pedotransfer function and soil variables from a 147 French Soil database. In a second step, the risk approach was tested to assess graduated soil N2O 148 emissions risk based on the combination of vulnerability and hazard. A former dataset was also used 149 to assess the validity of the soil risk classification. Therefore, this study aims to contribute and 150 improve existing tools and approaches to provide at decision-scale N₂O emission maps from existing 151 soil databases.

- 152 **2.** Materials and methods
- 153
- 154 2.1. The study area

The study area is a watershed in the upper valley of Loir River "Haut-Loir", located in French "Centre Val-de-Loire" region France, that has already been the support of several studies on direct and indirect N₂O emissions (Gu et al., 2013; Grossel et al., 2016; Billen et al., 2018, 2020). It extends over 3600 km² and includes seven agricultural regions: Perche, Faux Perche, Beauce, Beauce Dunoise, Orléanais, Val de Loire and Vallée de Loir (Figure 1). The four main regions (Perche, Faux Perche, Beauce, Beauce Dunoise) represent 90% of the study area and are covered by intensive croplands – usually wheat, barley, maize and rapeseed - that are subjected to high nitrogen inputs.





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Figure 1: Haut-Loir extension, study area

164 The Loir River consists in a natural limit between the Eastern Beauce/Beauce Dunoise regions and the 165 Western Perche/Faux Perche regions. For the purposes of this regional study, the soil classification was kept in its original repository (RP2008, Baize et al., 2009) described in the French database 166 167 (Figure 2). The correspondence between the RP2008 and the WRB soil classifications is given in the Appendix A. The match is not easy between the two systems of classification because a soil described 168 169 in RP2008 can have several matchings in WRB and vice versa. The correspondence depends on many 170 possibilities of qualifying soils that have not been further analysed in this study due to the lack of 171 representativeness at this regional scale.





173 Figure 2: Haut-Loir soils map. Soils are given in regional repository and the correspondence to WRB
174 is given in Appendix A.

175 The Western Perche and the Vallée du Loir Region are dominated by hydromorphic LUVISOLS and 176 PLANOSOLS, which are usually drained and limed for agriculture practices (Figure 2). 177 REDUCTISOLS are usually located near streams. In the Beauce/Beauce Dunoise regions, soils are 178 developed on limestone (CALCOSOLS, CALCISOLS and NEOLUVISOLS ...): they are more clayey 179 and exhibit a higher pH value. Agricultural soils in these Eastern areas are usually irrigated, which 180 allows maize plant in crop rotation. Orléanais forest region, in the Southwest part of the study area, 181 and the Val-de-Loire Region, are dominated by PLANOSOLS and REDOXISOLS. The white areas in 182 the soils map (Figure 2) correspond to undefined soil (urban areas) where there is no data in DoneSol.

183

184 2.2. The soil database

185 We have used a French Soil Geographical database on a scale of 1:250,000: "Référentiels Régionaux 186 Pédologiques", RRPs (Richer-de-Forges et al., 2019). RRPs are regional geographic databases 187 established from field surveys and observations by soil scientists. The data from RRPs are available to 188 users through a national standardized soil information storage system (DoneSol).

Donesol contains a list of Soil Typological Units (**STU**). In RP2008, STU are described by variables specifying the soil type and their properties (soil texture, CEC, pH, soil drainage, etc.). Soil natural drainage is coded from 1 (well-drained soils) to 9 (submerged soils) (Richer-de-Forges et al., 2019; *cf*. Table 1, supplementary material). This indicator provides information on the frequency of excess water in the soil.

At the scale of 1:250,000, it is not possible to delineate the STUs. Therefore, they are grouped into Soil Mapping Units (SMU) to form soil associations and to illustrate the functioning of pedological systems in landscapes. Each SMU corresponds to soil-landscape, i.e. a part of the mapped territory defined by specific pedology, hydrogeology, topology and / or land use. It has a known shape and location and is represented by one or more polygons in a geometrical dataset. Oppositely, STU cannot be precisely located within SMU. Soil type (STU) can be identified within SMU and is specified as a
percentage of SMU area. As a result, RRPs consists of both a geometrical dataset defining SMU and a
semantic dataset which links attribute values, including STU and soil variables, to the SMUs. It is the
same principle than for Soil Geographical Database of Europe, well-illustrated in the supplementary
Figure 1.

For display purpose, the SMU properties are represented with either the dominant STU, or a weighted average of STU areas. Both methods were tested in this study. Database structure is explained in the following link:

207 (https://esdac.jrc.ec.europa.eu/ESDB_Archive/ESDBv2/esdb/sgdbe/metadata/purity_maps/purity.htm.

208

209 2.3. R-max index

The r-max index, indicative of the capacity of a soil to reduce N_2O to N_2 , was calculated for each STU by using soil variables (CEC, pH and clay content) from the DoneSol database according to the following function (Henault et al., 2019 and ISO/TS 20131-2 norm):

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$$r-max = -0.4 pH + 0.026 CEC - 0.001 clay + 3.13 (r = 0.88)$$

where pH is evaluated on an air-dried sample suspended in water according to the NF ISO 10390 norm, CEC is evaluated on a soil sample extract using a cobalt-hexamine solution (Orsini and Rémi, 1976) according to the NF X 31-130 norm, and clay represents the clay content (g.g⁻¹) measured on a soil sample without decarbonation by using the Robinson pipette method according to the NF X 31-107 norm. The r-max values are limited to 1.2.

According to Hénault et al., 2019, soils with an *r-max* > 0.8 have a very low capacity to reduce N₂O, soils with *r-max* < 0.4 are able to reduce N₂O and soils with an *r-max* value between 0.4 and 0.8 have an intermediate capacity to reduce N₂O. Soil pH explains most of the *r-max* index variability (61%): soils with pH < 6.4 have usually *r-max* > 0.8, and soils with pH > 6.8 have r-max < 0.4, (Hénault et al., 2019).

- 224 2.4. Definition of N_2O emission risk
- 225 Risk of N₂O emission was based on Hazard, Vulnerability and Exposure as suggested in literature
- 226 (Crichton, 1999; Wolf, 2012; Lavell et al., 2012).



227

228 Figure 3: representation of N_2O emission risk, inspired by core concept of SREX IPCC, 2012

In our case (Figure 3) Vulnerability corresponds to the soil inability to reduce N_2O , natural Hazard is the probability that a situation of excess water occurs, and Exposure corresponds to N fertilization by farmers, leading to an increase in available mineral N into the soil. Hazard can be predicted thanks to precipitations or soil water content measured by in situ sensors. Exposure could be limited by decreasing N inputs. Exposure depends on land use: croplands were considered as the only ones that are subject to nitrogen inputs related to fertilization. For urban area or forest, Exposure is zero.



237 Three classes of Vulnerability were defined: Low Vulnerability (LV) for r-max < 0.4, Moderate Vulnerability (MV) for 0.4<r-max<0.8 and High Vulnerability (HV) for r-max >0.8. Hazard, i.e. 238 239 probability of excess water in soils, depends not only on precipitations but also on soil type. Soil 240 drainage class was thus considered to identify areas where excess water may occur. Three classes of 241 Hazards were similarly defined: Low Hazard (LH) for DoneSol soil drain classes 1, 2 and 3, Moderate 242 Hazard (MH) for classes 4, 5 and 6 and High Hazard (HH) for classes 7, 8 and 9. Finally, we defined 243 risk by crossing vulnerability with hazard (Figure 4). However, hazard and vulnerability, as defined, 244 are not controlling N2O emission risk in the same way. Excess water controls the occurrence of 245 denitrification, i.e. N₂O production in soils. The soil capacity to reduce N₂O in N₂ is important only if 246 denitrification and N₂O production can occur, i.e. if there is significant hazard. This is why hazard was 247 considered to have a higher control on risk than vulnerability and the figure 4 is not fully symmetrical. 248 In other words, moderate Risk (MR) corresponds at situations of Moderate Hazard with Moderate or 249 High Vulnerabilities and High Risk (HR) corresponds at situations of High Hazard with Moderate or 250 High Vulnerabilities.

Last four risk categories were defined to suggest different mitigation strategies. Vulnerability can be reduced by actions of mitigation. For example, liming soils raises the pH and increases the soil's ability to reduce N₂O (Henault et al., 2019). Categories 1 (moderate risk) and 3 (high risk) correspond to situations of moderate vulnerability that can mostly be mitigated by liming soil when pH < 6.8. Categories 2 and 4 correspond respectively to Moderate Risk and High Risk that can be reduced by liming soil when pH < 6.4 and that further requires special precautions when supplying nitrogen in soil (dose reduction or taking account soil water condition).

258 2.5 Validation data

 N_2O emission measurements from previous studies (Hénault et al., 2005; Franqueville et al., 2018 and other unpublished studies) were used to validate the present approach. These measurements were carried out over thirteen study sites included in our study area "Haut-Loir". Thus, N₂O emissions and soil properties are available from direct measurements for one CALCISOLS, six LUVISOLS, two BRUNISOLS and four COLLUVIOSOLS. N₂O measurements were done by static chamber with a frequency varying from once per week to once per month.

All plots were cropped with winter cereals and fertilized with mineral N but at different timing, splitting and amount. Therefore, to compare sites, N_2O emissions were cumulated from the last date before first fertilization to one month after the last fertilization. N_2O peaks generally occur in the weeks following N inputs so this may encompass most of the fertilization effect. The ratio of cumulative emission during post-fertilization period to the N input amount was then calculated for all sites.

271 Measured r-max values following the protocol of Hénault et al. (2019) were reported when available 272 (measured r-max index). A Calc. r-max index was calculated from soil properties measured on in situ 273 soil samples during the studies and STU r-max index was calculated from the Donesol values of the 274 map soil STU. Drainage classes were inferred from Donesol database. This allowed to assess hazard 275 and vulnerability and to calculate a risk class for each site.

276

277 3. Results and discussi

- 278
- 279 3.1. Application of the *r-max* function at STU and SMU resolution
- 280 3.1.1.*r-max* index computed by STU

DoneSol semantic database was used to infer the *r-max* values for all STU with the values of clay.
CEC and pH (85% of STU). This allowed to assess an *r-max* value (Table 1) for each soil type of the

- study site and thus infer its vulnerability typology (ability to reduce N_2O to N_2).
- Table 1: r-max mean value by soil type and associated standard deviation (std). number (nb) of values
 in each STU and SMU. representativeness in study site (% area) and vulnerability typology.

Soil type (RP2008)	nb STU	r- max	r- max	% area	nb SMU	Vulnerability
		mean	std			

CALCOSOLS (CALCO)	23	0.11	0.13	10	25	LV
RENDOSOLS (RENDO)	11	0.14	0.14	3	22	LV
RENDISOLS (RENDI)	5	0.17	0.16	1	10	LV
HISTOSOLS* (HIST)	1	0.25		<1	1	LV
CALCISOLS (CALCI)	18	0.29	0.19	6	26	LV
FLUVIOSOLS (FLUV)	19	0.42	0.26	<1	9	MV
PEYROSOLS (PEYR)	1	0.44		<1	1	MV
COLLUVIOSOLS (COLL)	10	0.51	0.36	1	7	MV
NEOLUVISOLS (NEO)	18	0.58	0.21	12	20	MV
BRUNISOLS* (BRUN)	51	0.61	0.31	14	45	MV
ARENOSOLS (ARE)	1	0.62		<1	2	MV
PELOSOLS (PEL)	3	0.63	0.10	<1	2	MV
LUVISOLS (LUV)	50	0.64	0.22	28	32	MV
FERSIALSOLS (FER)	1	0.74		<1	1	MV
PLANOSOLS (PLANO)	10	0.78	0.09	8	15	MV
REDOXISOLS (REDOX)	6	0.80	0.37	2	11	HV
VERTISOLS (VERT)	1	0.86		<1	1	HV
REDUCTISOLS (REDUCT)	5	0.88	0.28	1	3	HV
ALOCRISOLS (ALO)	1	1.20		<1	1	HV
PODZOSOLS (PODZ)	2	1.20	0.00	<1	2	HV

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The *r-max* mean values vary from 0.11 (CALCOSOLS, carbonated soil from the surface) to 1.20 (PODZOSOLS, acidic soils). Soil types FERSIALSOLS, HISTOSOLS, ARENOSOLS, VERTISOLS and ALOCRISOLS are less encountered in the study area, thus their *r-max* values must be further confirmed.

The soils with the lowest *r-max* are soils developed on limestone (RENDOSOLS, CALCOSOLS, RENDISOLS and CALCISOLS). These soils have an *r-max* under 0.4, so they are able to reduce N₂O. They cover 20% of the Haut-Loir surface and they are mostly to the Eastern of the site (Beauce/Beauce dunoise). For the HISTOSOLS the *r-max* value is 0.25. As HISTOSOLS correspond to peat soils (organic soils) and are often acidic, farmed organic soils appear to emit exceptionally large amounts of N₂O (Kasimir-Klemedtsson et al., 1997). However, in this study the only HISTOSOLS is a eutrophic-peat with pH > 8. All the other soil types present a mean of *r-max* over 0.4, and some of them are over 0.8 (REDUCTISOLS, REDOXISOLS, VERTISOLS, PODZOSOLS and ALOCRISOLS, for 5% of the study site) and therefore not able to reduce N_2O (HV). Over 60 % of soil surface are classed in MV.

The BRUNISOLS (14 % of the study area) show *r-max* values ranging from 0 to 1.2. In fact, there are two large categories of BRUNISOLS: Eutric BRUNISOLS and Dystric BRUNISOLS Dystric soils have a base saturation (S/CEC: S being the sum of exchangeable cations (Ca²⁺, Mg²⁺, K⁺ and Na⁺)) at pH=7 of less than 50 % whereas Eutric soil have a base saturation at pH=7 of 50 % or more (Baize et al., 2009). This soil attribute depends on the CEC and therefore has an influence on the *r-max* value. Dystric BRUNISOLS have an *r-max* mean value upper than 0.8 and Eutric BRUNISOL have a *r-max* value about 0.59, i.e. in the intermediate class.

309 There is also a large variability in *r-max* values of hydromorphic soils (COLLUVIOSOLS, 310 FLUVIOSOLS, REDOXISOLS and REDUCTISOLS), because these soils could be more or less 311 clayey and more or less acidic.

The value of the *r-max* seems to follow a growth in the direction of soil evolution through the lateralization processes of clay lixiviation and acidification. Low-evolved soils (RENDOSOLS, RENDISOLS, CALCOSOLS and CALCISOLS) have the ability to reduce N_2O to N_2 , then soils that move towards BRUNISOLS, LUVISOLS, PLANOSOLS lose their ability to reduce N_2O and finally REDUCTISOLS and PODZOSOLS no longer reduce N_2O at all in N_2 .

This soil evolution is described in soil Atlas of Europe in WRB classification. Cambisols degrade 317 318 because of vertical water erosion. The continuous leaching moves the calcium carbonate front further 319 downwards, the pH drops to about 6 and clay illuviation starts to become rich Luvisol. However, the 320 leaching will continuously remove the base elements from the soil. This will make the profile so acid 321 that it will be classified as an Alisol. At this stage the soil is so acid that the clay in the illuviated 322 horizon will disintegrate or be redistributed to other parts of the profile and tongues of silt and sand 323 will cut into the clay illuviated horizon. This is referred to as an Albeluvisol. Finally, the leaching will 324 enable an iron pan to develop and the soil turns into a Podzol.

325 3.1.2.r-max aggregation by SMU

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326 SMU r-max maps joining data from RRPs and Donesol were carried out with the r-max mean of all 327 STU contained in the SMU weighted by their area (Fig. 5a) and using the soil variables of dominant STU (Fig. 5b). There are many similarities between the two maps. The difference between Eastern and 328 329 Western regions can be explained by the presence of soils developed on limestone in Beauce/ Beauce Dunoise (CALCOSOLS, RENDOSOLS, RENDISOLS, CALCISOLS) and the more acidic soils in 330 331 Western regions. Overall Western soils are not able to reduce N_2O . The highest *r*-max values are located near the streams and in watershed heads of the Western-Perche/Faux Perche region 332 (REDUCTISOLS and LUVISOLS). 333

Figures 5c and 5d correspond, respectively, to the standard deviation calculated in the SMU and to the representativeness of the dominant soil in the SMU. The maps show SMU with an *r-max* values > 0.8 in northeast (Beauce) and in southeast (Orléanais). In these areas, the *r-max* standard deviation is > 0.4 (Figure 5d). This suggests a large variation of *r-max* within the SMU due to differences between *r-max* from grouped STU.



Figure 5: r-max maps and related standard deviation at study site (Haut-Loir) (respectively with mean
and standard-deviation of all STU per SMU: 5a and 5c; and dominant STU values, 5b and 5d). See

text for more details.

- 343 SMU aggregation allows to represent spatially the *r-max* at the expense of accuracy. The mean value
- tends to smooth out extreme values and the dominant STU value is not always representative.
- 345
- 346 3.2. Risk assessment
- 347 3.2.1. Vulnerability and Hazard
- 348 Figure 6 exhibits the percentage of area of each SMU corresponding to the different Vulnerability and
- 349 Hazard typologies. This area was estimated based on vulnerability and hazard of the STUs forming the
- 350 SMU.



352 Figure 6: Vulnerability and Hazard maps estimated at STU scale and expressed in percentage of SMU

area

353

These maps allow to detect where the most vulnerable soils are located and those subject to the greatest hazards. 15% of soil surface is not classified because of missing values. 29% of soil surface from study site are classified in Low Vulnerability, 44% in Moderate Vulnerability and 12% in High Vulnerability. 49% of soil surface are classified in Low Hazard, 35% in Moderate Hazard and 1% in High Hazard.

Soils with Low Vulnerability and Hazard are mostly located in Eastern Beauce/Beauce Dunoise. Soils
with Moderate Vulnerability and Hazard are mostly located in Western Perce/Faux-Perche and
Orléanais and soils with High Vulnerability and Hazard are located in valleys.

362 Hazard and Vulnerability areas are quite similar. Non-vulnerable soils, therefore able to reduce N_2O to 363 N_2 , seems not to have water excess characteristics. Conversely, vulnerable soils (MV and HV) are 364 generally in a situation of excess soil water (MH and HH). Indeed, excess water in the soil and 365 leaching induce redox processes and increase the soil acidity (Van Breemen and Buurman, 2002), so 366 these that two components are not always independent.

There are still a few special cases: the heads of watersheds on the Western side are classified in HV and LH. There is also an area in North of the Beauce region that is classified in HV (because of low pH value) and which is classified largely in LH.

370 3.2.2. Risk assessment by soil type

371 The risk of N_2O emission was assessed according to the soil type. The results are shown in Figure 7.



372

Figure 7: risk by soil type based on their Vulnerability (mean r-max in x-axis) and Hazard ranges
(mean drainage class in y-axis)). Bars indicate the min-max values of both r-max values and drainage

375 codes for each soil type. For clarity only the first letters of the name of soil types is given; see Table 2
376 and text for the full name.

377

378 Only REDUCTISOLS are in risk situation "4" and some of the FLUVIOSOLS which may be in a 379 significant situation of excess water are in risk situation "3". These two soil types are located in 380 wetlands that are currently protected from excessive nitrogen inputs. They are mostly occupied by 381 grasslands because the excess water does not allow cultivation.

Soils developped on limestone (CALCISOLS, CALCOSOLS, RENDISOLS and RENDOSOLS) do not present any risk of N_2O emissions. HISTOSOLS, PEYROSOLS, VERTISOLS and ALOCRISOLS have no risk either, but there is only one value available to characterize them. PODZOSOLS have a High Vulnerability but the mean value of soil drain class is 3, thus the risk is between Low and Moderate. Podzosols are very poor and very acidic soils that are not conducive to agriculture.

All the others soils have a mid point in risk situation class "1" or "2". As soil types are generaly 388 389 composed of several STU, some STU may be at risk of N₂O emission and some others not, which is illustrated in the Figure 7 by bars crossing the dashed risk line. Some of BRUNISOLS, 390 COLLUVIOSOLS, LUVISOLS, NEOLUVISOLS, PLANOSOLS and REDOXISOLS can be in 391 392 moderate risk category (situations 1 or 2) depending on their *r-max* values and usually of acidity. 393 High-risk situations of N₂O emissions are not necessarily found in cultivated areas and are therefore 394 not subject to high nitrogen Exposure. Indeed, very moist and acidic soils are not favourable to 395 agriculture.

396

3.2.3. Validation of the approach using a former dataset

397

398

- 399 Table 2 shows a very good consistency between N₂O emission and Calc. *r-max* index. However, some
- 400 discrepancy exists between Calc. r-max index and STU r-max index (Table 2). This is owing to soil
- 401 map resolution. Nevertheless, all soil types are within the same risk class as shown in Figure 7.

402 Table 2: Sites used for the validation and the measured properties during the field campaigns. The 3 first sites were taken from Hénault et al. (2005). SP sites were taken from

Franqueville et al. (2018). ND4 is the same site as presented in Grossel et al. (2016) but flux data are unpublished. See these studies for more details. Note that SP5, SP6 and 404 ND4 were sampled in both 2014 and 2015. SP7, SP8 and INRAE data are unpublished. Last column indicates the r-max index value calculated with the pedotransfer function

of Hénault et al. (2019). Class risk estimated with the map soil typology.

			Donesol database													
Site	Region	Period	N ₂ O emission (g-N /ha)	N input (kg N/ha)	Measured r-max index	pН	CEC (cmol +.kg ⁻¹)	Clay (g.kg ⁻ ¹)	Calcultated r-max index	STU name	pН	CEC (cmol +.kg ⁻¹)	Clay (g.kg ⁻¹)	STU r-max index	Drain class	classr isk
Villamblain (1999)	Beauce Dunoise	Feb - June 1999	517	230	0.2	7.9	22.8	334	0.23	CALCISOLS	8	20.8	341	0.13	2	0
La Saussaye (1999)	Beauce	Feb - June 1999	376	164	0.2	7.8	16.5	242	0.2	BRUNISOLS	6.6	9.6	175	0.56	2	0
Arrou (1999)	Faux- Perche	Feb - June 1999	2855	173	0.6	6.23	2.9	50	0.66	LUVISOLS	6.7	9	140	0.54	4	1
SP1 (2014)	Faux- Perche	Feb - May 2014	696	142		7.1	7.24	125	0.35	LUVISOLS	6.7	9	140	0.54	4	1
SP3 (2014)	Faux- Perche	Feb - May 2014	950	140		6.8	9.82	181	0.48	COLLUVIOSOLS	6.4	12.7	250	0.65	5	1
SP5 (2014)	Faux- Perche	Feb - April 2014	986	170		7	9.11	145	0.42	LUVISOLS	6.7	9	140	0.54	4	1
SP6 (2014)	Faux- Perche	Feb - April 2014	2034	175		6.3	8.06	237	0.58	COLLUVIOSOLS	6.3	8.1	230	0.59	5	1
ND4 (2014)	Faux- Perche	Feb - April 2014	2781	175	0.66	6.3	6.81	141	0.65	COLLUVIOSOLS	6.4	12.7	250	0.65	5	1
SP2 (2015)	Faux- Perche	Feb - May 2015	740	231		6.4	6.82	140	0.61	LUVISOLS	6.7	9	140	0.54	4	1
SP4 (2015)	Faux- Perche	Feb - May 2015	933	220		6.5	9.82	137	0.65	COLLUVIOSOLS	6.4	12.7	250	0.65	5	1
SP5 (2015)	Faux- Perche	Feb - May 2015	314	230		7	9.11	145	0.42	LUVISOLS	6.7	9	140	0.54	4	1
SP6 (2015)	Faux- Perche	Feb - May 2015	293	230		6.3	8.06	237	0.58	COLLUVIOSOLS	6.3	8.1	230	0.59	5	1
ND4 (2015)	Faux- Perche	Feb - May 2015	2118	230	0.66	6.3	6.81	141	0.65	COLLUVIOSOLS	6.4	12.7	250	0.65	5	1
SP7 (2018)	Faux- Perche	Feb - May 2018	1550	240		7.2	9.7	118	0.4	LUVISOLS	6.7	9	140	0.54	4	1
SP8 (2018)	Faux- Perche	Feb - May 2018	1126	234		6.6	8.8	118	0.58	LUVISOLS	6.7	9	140	0.54	4	1
INRAE (2018)	Val de Loire	May - June 2018	200	100	0.61	6.23	2.9	50	0.66	BRUNISOLS	4.2	6.1	48	1.2	2	0



408 Figure 9 : r-max index calculated based on measured soil properties versus emission ratio during
409 post-fertilization period.

The risk class for each site was estimated (table 2). Only three sites were classified as risk class 0 (no risk). One of them presented both low hazard and low vulnerability (Villamblain site) while the two others presented medium vulnerability but low hazard (good drainage class) resulting in low emission risk. For one of these sites, (La Saussaye) this was not consistent with direct observations because a small r-max index was measured.

415 A risk class 1 was found for ten sites, corresponding to thirteen N_2O emission values (three sites were 416 sampled in both 2024 and 2015). This could be explained by the fact that an area known for its 417 emissions is usually selected for such studies. There may therefore be a bias in favor of soils at risk 418 when choosing sites. However, no risk class greater than 1 was found.

419 To assess if soil classified as "at risk" indeed present largest N_2O emission, Figure 10 shows the ratio 420 of cumulated N_2O emission on N inputs during fertilization and post-fertilization period as a function 421 of class risk. During wet seasons, the ratio of N_2O emission on N input was smaller on sites 422 presenting no risk (about 0.2%) than on sites presenting a risk class 1. Sites having a risk class 1 423 showed a large variability of the emission ratio, but it was always larger than 0.4%. In 2015, which 424 was a rather dry year, only sites having a risk class 1 were studied. The emission ratio also presented a 425 large variability but it was smaller than during wet seasons and some sites even presented emission 426 ratio as low as the no risk sites during wet years. This is consistent with the hypothesis that risk is 427 associated to hazard more than vulnerability because in dry conditions, even in hydromorphic soils, 428 there is little denitrification.

429



430

Figure 10: N₂O emission ratio versus soil risk class. Emission ratio is calculated as the ratio of cumulated emission of N₂O during fertilization and post-fertilization period on N inputs and soil risk class is assessed through Donesol variables of the corresponding STU (see methodology part for more details). Left: observations made during wet climatic years, right: observations during normal to a dry climatic year. Emissions were cumulated over the fertilization periods, thus corresponding to different intervals (see Table 2).

438 Figure 8 (top) presents the percentage of area that present a risk of N₂O emissions, and on the other





440

Figure 8: Top. map of the relative area presenting N₂O emission risk; bottom: maps of relative area of
each emission risk categories 1, 2, 3 and 4. For risk category definition, see Figure 5.

443 The risk situation is undefined for 15% of the total area. 53% of the surface present no risk of N_2O 444 emissions conversely to 32% of the total area. These 32 % can be split into 4 situations: 24 % in 1, 6% in 2, less than 1% in 3 and 1% in 4. Most of these risky soils are located in the Western Perche/Faux
Perche region, where 12% of the surface is covered by forest. Part of risky soils is also located in the
Orleans forest (Orléanais region), but these soils are not exposed to nitrogen inputs, risk does not exist
without exposure.

449 3.2.5. Uncertainties and strengths of the present approach

450 This approach of mapping emission risk can present several limitations. Firstly, as already written for 451 hazard and vulnerability maps, SMU aggregation entails uncertainties on the final risk map. To check 452 how reliable the two aggregation methods were, the risk for validation site was also estimated based 453 on SMU and not true STU (see supplementary material). Both SMU aggregation methods gave the 454 same risk class than the true STU corresponding to the sites. The methodology used for soil 455 classification also present uncertainties. The protocol for the *r-max* index measurements is based on 456 incubation with acetylene. The acetylene method can underestimate denitrification and ratio 457 $N_2O/(N_2O+N_2)$ because of several reasons, e.g. low diffusion of acetylene in intact soils and inhibition 458 of nitrification in field conditions (Groffman et al., 2006) so field assessment may be biased. The 459 present index is measured in artificial conditions: soil slurry amended with nitrate under agitation: 460 these conditions provide an index of the soil capacity of reduction to N_2 and not a direct measurement. 461 Reduction of N_2O to N_2 can also be influenced in the fields by the soil nitrate and carbon availability 462 (Senbayram et al., 2012). However, the *r-max* index measured in the laboratory has been shown to relate well with field N₂O emissions (Hénault et al., 2005; Hénault et al., 2019). Last, only natural 463 464 drainage class from Donesol database was considered to define the hazard. Soil hydromorphy effect on 465 N₂O emission can however be highly impacted by management practices: e.g. tile-drainage (Grossel et al., 2016), tillage (Rochette et al., 2008), soil compaction (Pulido-Moncada et al., 2022). 466

The approach was evaluated by comparison with a limited database from in situ measurements and it would be interesting to have further field data for validation. Moreover, field data also present uncertainties : emissions were measured by manual static chambers and cumulative emissions has an uncertainty linked to the frequency of measurements (Smith and Dobbie, 2001). Observed variability 471 is linked to the soil moisture dynamics, which is controlled not only by the precipitation regime but 472 also the vegetation, tillage, and soil hydromorphy itself which can be due to the presence of a deep 473 clay layer, position in topography (foot slopes) or contact with a water table. This can be illustrated by 474 the site 5 (Franqueville et al., 2018) which was measured in 2014 and 2015. It was close to an 475 intermittent river and soil hydromorphy is due to this vicinity (river water table). In spring 2015 the 476 river dried out and N₂O emissions ratio on N input was very low, while it was large in spring 2014. 477 Last the variability of emissions is also controlled by the timing of fertilization and precipitations. The 478 classification does not discriminate all field conditions but observations are consistent with the 479 assessed soil classification for N₂O emissions risk, suggesting that it can help distinguishing between 480 risk level 0 and 1.

481 N₂O emissions are controlled by a complex interplay of many factors, resulting in large variations both 482 in time and space. N substrate is the main factor so many mitigation solutions have focused on 483 applying N at optimal rate to limit surplus, using enhanced efficiency fertilizers, including nitrification 484 inhibitors or introducing legumes in rotations (Luo et al., 2019; Kanter et al., 2020; Wagner Riddle et 485 al., 2020). Although some solutions will benefit to any soil or climate type (such as health diet habit, 486 Luo et al., 2019), identifying the riskiest areas for N₂O emissions is also needed to target mitigation 487 efforts (Cui et al., 2021). Site-specific management is proposed to mitigate local hotspots of N₂O 488 emissions but it has yet to be tested how this approach can apply at regional scale (Wagner-Riddle et 489 al., 2020). This study proposes thus an approach to identify possible risk areas. This approach is based 490 especially on a risk classification by soil types; soil type has indeed been long recognized as a control 491 factor of N₂O emission (Robertson 1989).

Identifying the risk factors could help proposing mitigation strategies. For 3/4 of the risky situations (risk classes 1 + 3), N₂O emissions could be mitigated by regularly liming soil to maintain a pH around 6.8, as suggested by Hénault et al. (2019). Liming can have beneficial effects by reducing N₂O emissions, while it can also increase agronomic risk (defficiency) and CO₂ emissions, but a recent meta-analysis suggested that, because of general yield increase, it may be beneficial (Zhang et al., 2022). Management based on liming should therefore still be assessed by local studies (Hénault et al., 498 2019) and the present approach can also serve to guide where to conduct such studies. A third of other 499 soils (risks 2 and 4), require a liming so-called "redress" action to avoid any risk. A soil drainage 500 action does not prevent temporary water excess, but just limit this duration. It is best to avoid exposing 501 soils to risk in too wet soil situations by not providing nitrogen. Farmers can predict these situations 502 through the weather forecast or using soil moisture sensors. Theses situations are located at the edge of 503 streams (The Loir and its tributaries), in areas with REDUCTISOLS and FLUVIOSOLS. It is not 504 advisable to fertilize these soils areas, which are often classified as wetlands and which also cause 505 problems with nitrate pollution.

506 The patterns of the risk map (Figure 8) are consistent with those of Lugato et al. (2017), who mapped 507 mean N₂O emission simulated on five years (supplementary material). Their map also showed two contrasting N₂O emission areas with values from 1.09 kg N ha⁻¹ yr⁻¹ to 3.8 kg N ha⁻¹ yr⁻¹ for 2010 to 508 509 2014 at Haut-Loir. The added value of current paper is that it proposes maps of emission risk provided 510 by soil types, rather than N_2O emission, which are dependent on temporal variables such as 511 precipitation regimes and agricultural practices. This enables also to propose action to be taken 512 according to the risk situation. The *r*-max value (computed from soil clay content, CEC and pH) 513 associated with a soil water excess indicator, available in French soil database, seems to be an efficient 514 approach to define soil situations that require special care and help farmer to identify risky situation.

515

516 Conclusion

A methodology to map N_2O emission risk at regional scale based on soil properties was developed. Risk was defined by crossing a "vulnerability", defined by the low capacity of soil to reduce N_2O in N_2 during denitrification, and "hazard", defined by the probability to have water excess and directly linked to soil drainage class. In the Haut-Loir watershed, 32% of soils presented N_2O emission risks (when exposed to nitrogen fertilization), of which 75% could be mitigated by liming. Some soils (mainly the REDUCTISOLS in the valleys and some hydromorphic LUVISOLS), covering 7% of the watershed area, would require moreover special attention in nitrogen inputs. As the method is based

- 524 on knowledge of well-known factors controlling N₂O production and reduction by denitrification and
- 525 as these data are accessible in soil databases, i.e. drainage class, pH, CEC and clay content, it could be
- 526 also applied to other regions. These risk maps can allow decision-makers to identify agricultural areas
- 527 that require special precautions to reduce agricultural N₂O emissions.

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533 Appendix A : soil correspondance RP 2008 to WRB 2006

RP 2008	WRB 2006
ALOCRISOLS	Cambisols Hyperdystric
ARENOSOLS	Arenosols
BRUNISOLS	Cambisols Eutric or Dystric
CALCISOLS	Cambisols Hypereutric
CALCOSOLS	Cambisols Calcaric
COLLUVIOSOLS	Colluvic Regosols
FERSIALSOLS	Haplic Luvisols
FLUVIOSOLS	Fluvisols
HISTOSOLS	Histosols
LUVISOLS	Haplic Luvisols or Haplic Albeluvisols or Luvisols
NEOLUVISOLS	Luvic Cambisols
PELOSOLS	Epistagnic regosols or Vertic Cambisols
PEYROSOLS	Hyperskelectic Leptosols or Hyperskelectic Podzols
PLANOSOLS	Planosols
PODZOSOLS	Podzols
REDOXISOLS	Stagnosols
REDUCTISOLS	Gleysols
RENDISOLS	Epileptic Cambisols Calcaric
RENDOSOLS	Epileptic Cambisols Hypereutric
VERTISOLS	Vertisols

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